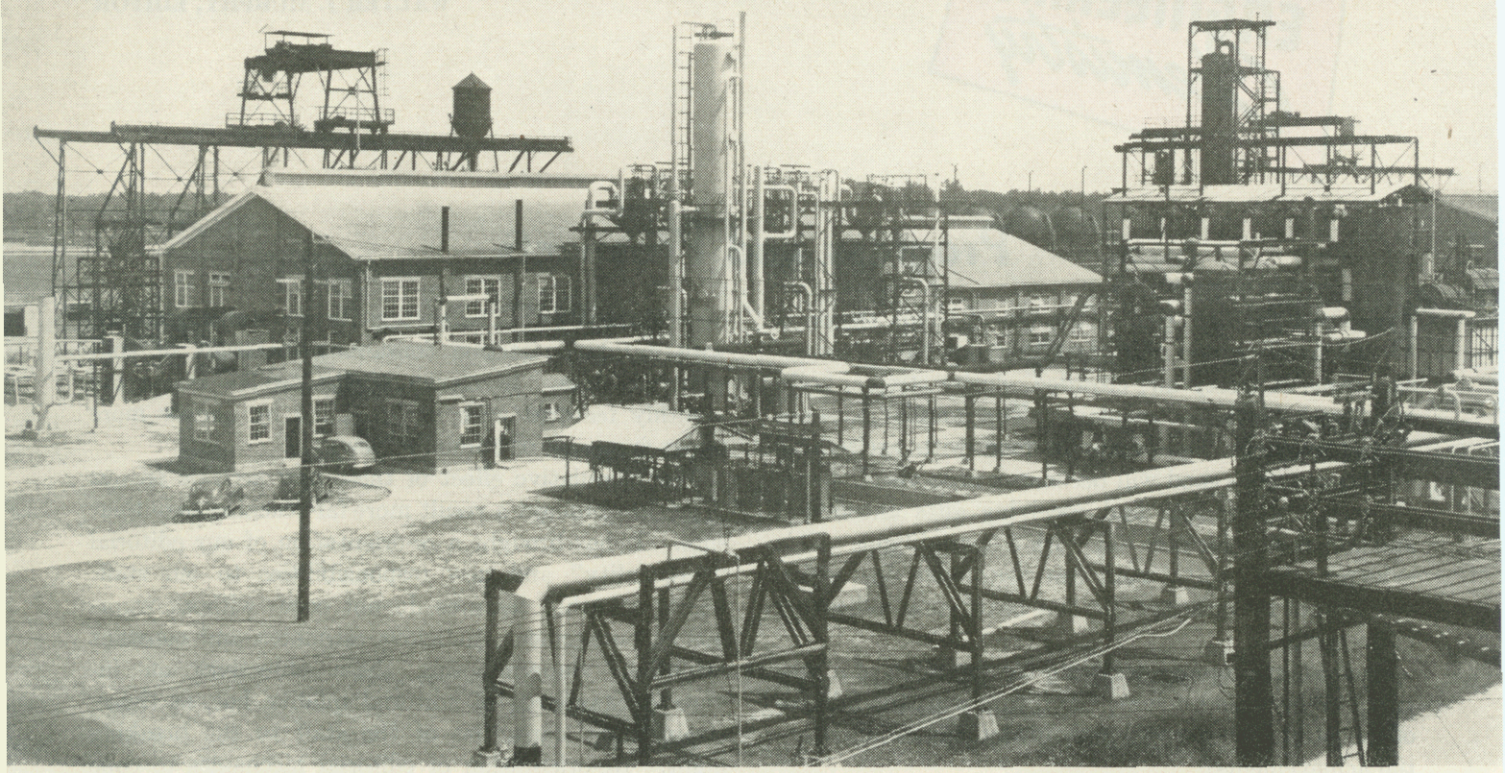
Synthetic Methanol Production



A Staff-Industry Collaborative Report . . .

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ONE of the most phenomenal growths in the record of the American chemical industry is that experienced in the manufacture of synthetic methanol during the past 20 years. Keyed to that growth, both as cause and effect, is the expansion of formaldehyde production and the advent of the formaldehyde type plastics. Oxidation of methanol to formaldehyde accounts for almost half of the total production. This percentage has remained relatively constant throughout the history of methanol production. However, steadily increasing application of the basic phenolformaldehyde type plastics has increased the actual tonnage of methanol used for this purpose manyfold during the past two decades. Two thirds of the remaining production now is used as automobile antifreeze and this application is expected to expand as methanol production capacity catches up with excess demand (*34*).

Unlike its use in formaldehyde production, the use of methanol in automobile radiators is a fairly recent application. Although it has a lower boiling point than the previously used denatured alcohol, its lower molecular weight gives it less partial pressure so that it does not boil away as fast as the higher alcohol. At the present time a considerable volume of ethanol is still being used for this purpose. However, methanol producers predict that once they achieve adequate production they will split the antifreeze market about 65 to 35 with ethylene glycol, assuming that glycol prices remain steady. If the price is depressed by the new production provided by Wyandotte Chemical Company, E. I. du Pont de Nemours & Company, and Jefferson Chemical Company, glycol may claim a larger percentage of the market. If on the other hand, prices follow the upward trend, use of methanol may be favored.

Some observers feel that ethanol producers will not relinquish this major market without a struggle. However, they must overcome a 25- to 50-cent per gallon price differential. One straw in the wind is the withdrawal of Du Pont's ethanol antifreeze from the market. Beverage alcohol producers may retain an entry into the market and may even enter into price competition with methanol to retain a stabilizing market for surplus fermentation alcohol.

The recency of the antifreeze market is apparent from a comparison of percentage consumption figures for 1930 and 1947:

	Per Cent	
	1930 (*10*)	1947 (*11*)
Formaldehyde (production and stabilization)	41	44
Denaturant	31	5
Antifreeze	...	38
Miscellaneous and solvent	23[a]	13[b]
Dimethylaniline	5	...
Total	100	100

[a] Includes antifreeze.
[b] Includes dimethylaniline production.

HISTORY OF SYNTHETIC METHANOL

Thirty years ago there was no commercial production of synthetic methanol. The wood alcohol produced was made by the destructive distillation of wood waste by much the same procedure that Taylor used to obtain what he had named "pyroligneous ether" over a century before. Methanol was a special chemical used largely as a denaturant in ethyl alcohol. That portion of the 8,000,000 or 9,000,000 gallons produced annually which was used as a raw material for further synthesis went into the production of other special compounds which could absorb the post World War I price of almost a dollar a gallon.

The entire methanol synthesis process can be seen here. Natural gas enters by the overhead pipe line in the foreground, is reformed in the furnace at the right, cooled in the tall tower at center, compressed in the brick building, and converted to methanol on the converter line under the crane structure seen in left background. Purification is behind reformer furnace.

FOREIGN DEVELOPMENT

As long ago as 1905 Sabatier had stated the theoretical possibility of producing methanol by the catalytic combination of carbon monoxide and hydrogen but he had no way of determining the equilibrium of the reaction or the theoretical yield and he never succeeded in achieving the synthesis even on a laboratory scale. However, the problem was solved almost simultaneously about 15 years later by Patart in France and a group working at the Badische Anilin- und Sodafabrik. The German group had obtained a patent claiming the use of a mixture of zinc and chromium oxides as a catalyst for this synthesis in 1913, but it is accepted generally that the first workable process was covered by Patart's patent issued in 1921 (*23*). This patent claimed all metals, their oxides and salts, which are known to favor oxidation or hydrogenation, as catalysts for the reaction. Operating conditions were set at 300° to 600° C. and 2235 to 2940 pounds per square inch gage pressure with a hydrogen–carbon monoxide volume relation of two to one.

In spite of Patart's prior discovery it is not surprising that Badische Anilin- und Sodafabrik, having discovered and developed the Haber process (*1*), should have been able to put the first successful commercial methanol plant on the line in 1923. This plant operated at 100 atmospheres pressure and 400° C. and by the end of the year was producing 10 to 20 tons per day of synthetic methanol. During the first year of operation the product of this plant was sold, delivered in New York, duty paid, at 40 cents a gallon; this was less than half the going price for domestic wood alcohol.

SYNTHETIC METHANOL IN THE UNITED STATES

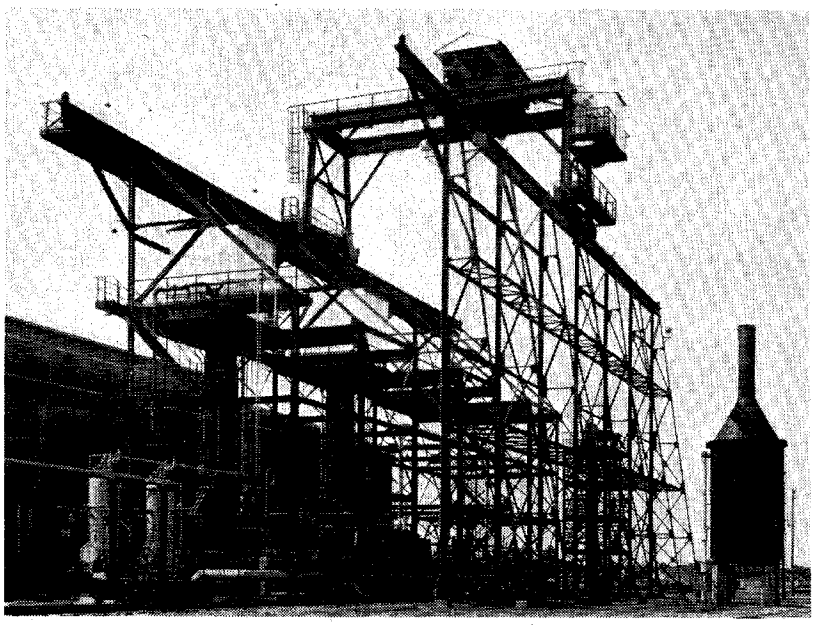
In less than 4 years, in the spring of 1927, synthetic methanol was being produced in the United States. The first unit in operation was located in Belle, W. Va., at the ammonia plant of Lazote, Inc., a Du Pont subsidiary. This first installation was essentially an experimental unit installed in conjunction with existing ammonia synthesis facilities. The ammonia synthesis gas containing about 1 to 2% carbon monoxide as an impurity was passed through the methanol converter as a purification step. Final traces of carbon monoxide were removed by methanation in a second converter. The production of this unit was absorbed completely within the Du Pont organization but it was announced as part of a program designed to supply the entire American demand for methanol.

The practice of running a single synthesis gas stream through both methanol and ammonia converters as in the original Du Pont plant is often considered to be the major contribution of American science to the technology of methanol synthesis (*10*). It is no longer used in this country but has been adopted widely throughout Europe.

In the summer of 1927, a few months after the Belle installation began production, Commercial Solvents Corporation announced the completion of a synthetic methanol plant at the Peoria works; this production was to triple the production of synthetic methanol in the United States. Also a by-product unit, this installation used fermentation gas from butyl alcohol–acetone production units as its raw material. This gas consisted almost entirely of 60% carbon dioxide and 40% hydrogen. The unit was constructed and operated originally for the production of ammonia. However, after operating less than a month, ammonia production was abandoned and the converters changed over to a unique catalyst which initiated the reaction:

$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O$$

The Peoria installation is believed to have been the first commercial application of high pressure synthesis from pure carbon dioxide and hydrogen. The converted methanol plant was an-



Two Converter Vessels Straddled by Gantry Crane, Sterlington Plant

(Right) Furnace used to heat gas during start-up

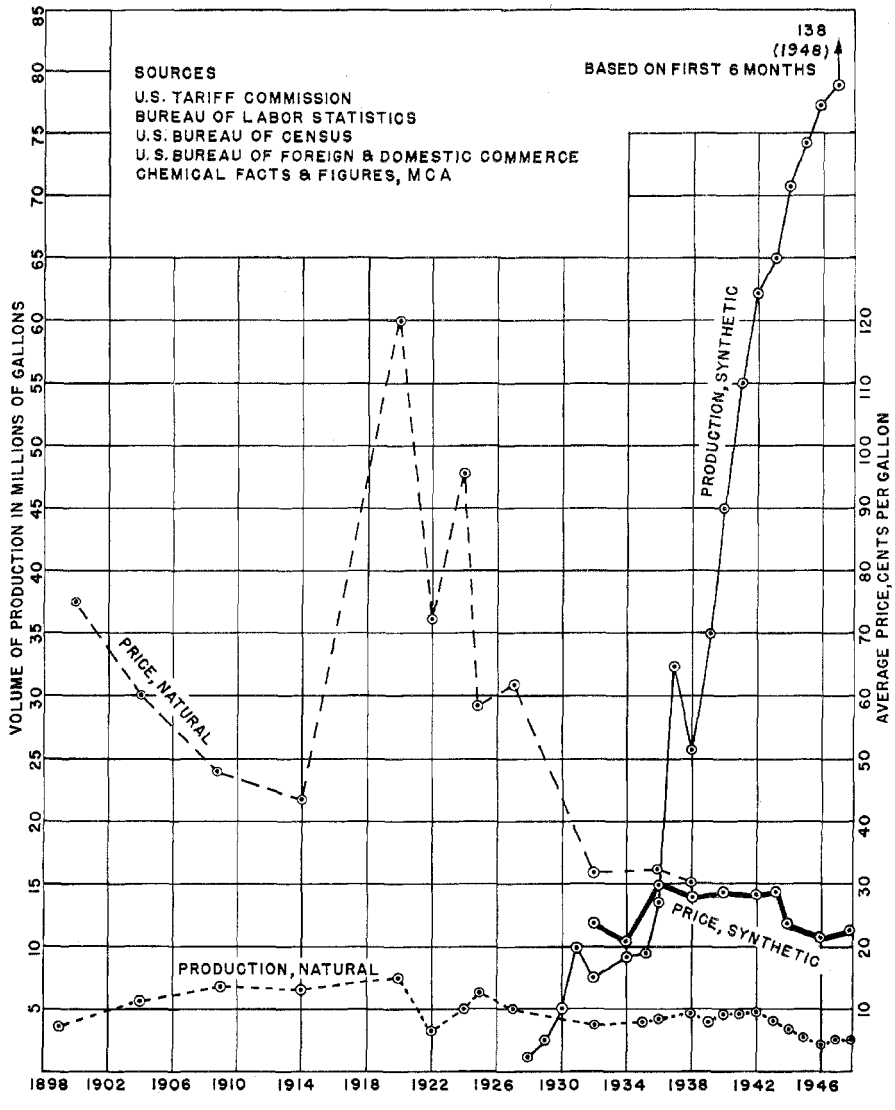

138
(1948)
BASED ON FIRST 6 MONTHS
SOURCES
U.S. TARIFF COMMISSION
BUREAU OF LABOR STATISTICS
U.S. BUREAU OF CENSUS
U.S. BUREAU OF FOREIGN & DOMESTIC COMMERCE
CHEMICAL FACTS & FIGURES, MCA
PRODUCTION, SYNTHETIC
PRICE, NATURAL
PRICE, SYNTHETIC
PRODUCTION, NATURAL
VOLUME OF PRODUCTION IN MILLIONS OF GALLONS
AVERAGE PRICE, CENTS PER GALLON
1898 1902 1906 1910 1914 1918 1922 1926 1930 1934 1938 1942 1946

Figure 1. Production and Price of Methanol Since 1898

nounced to have a capacity of about 1,300,000 gallons per year (*35*), this would set the capacity of the Du Pont plant at about 500,000 gallons per year.

Since the inception of the process the expansion of production capacity has been rapid and steady. By 1930 the domestic production of synthetic methanol had exceeded that of the natural product and importation from German producers had receded to negligible proportions. One million gallons of synthetic methanol were produced in 1927 by the two plants then in operation. In 1947 total production amounted to over 80,000,000 gallons (*15*).

POSTWAR EXPANSION OF CAPACITY

Post World War II expansion of production capacity has been phenomenal even for this traditionally fast growing industry. During the war years the War Production Board limited and eventually prohibited the use of methanol in automobile antifreeze. Even when relieved of this demand, which normally absorbed between 30 and 40% of the total production, methanol production was unable to keep up with the wartime requirements. Methanol is still scarce and its use in antifreeze has not reassumed its prewar volume. It has been estimated that in order to supply that portion of the antifreeze market which used methanol prior to World War II, production must be expanded to between 134,000,000 and 160,000,000 gallons per year in the next 3 or 4 years (*34*). This estimate, however, does not include allowances for any expansion in formaldehyde production. If present installations for the oxidation of methanol to formaldehyde could operate at full capacity they would consume 45,000,000 gallons of methanol annually. However, in 1947 they were able to obtain only about 30,000,000 gallons. Furthermore additional formaldehyde production capacity being constructed this year is expected to require another 15,000,000 gallons of methanol for raw material per year.

Capacity operation of formaldehyde production facilities is strongly dependent on availability of phenol, at present still scarce, since the major consumption of formaldehyde is in the manufacture of phenol-formaldehyde resins. However, the phenol situation is being improved so that it is safe to predict that the formaldehyde producers soon will require an additional 30,000,000 gallons of methanol per year; this brings the total demand for methanol into the area of 200,000,000 gallons annually.

In an attempt to keep pace with this burgeoning demand, methanol production capacity has been essentially doubled since 1945. In that year production was 77,000,000 gallons (*32*). In the first 6 months of 1948 nearly 70,000,000 gallons of methanol were produced (*31*). During this 6-month period only one of the new postwar plants was in dependable production. By the end of the year most of the postwar expansion program will have been completed. Therefore, it is safe to assume that production in the second half of 1948 will be substantially greater than that of the first 6 months. In 1945 only four companies were producing methanol synthetically and two of these companies, Du Pont and Carbide and Carbon Chemicals Corporation accounted for well over 90% of the production. In 1946 Celanese Corporation entered the field with a plant at Bishop, Tex., where butane and propane are oxidized to the alcohol by a novel process. During the past year Solvay Process Company, Spencer Chemical Company, and McCarthy Chemical Company also have undertaken methanol synthesis for the first time. In addition to these new entries into the field, the two pioneers in the field both have increased their capacity. Du Pont has constructed a new plant at Orange, Tex., which it is believed equals the older Belle, W. Va., plant in capacity and Commercial Solvents new Sterlington plant has more than four times the capacity of the company's expanded unit in Peoria. Three of the new units—those of Solvay, Spencer, and Commercial Solvents—are based upon surplus army ordnance plants. The Solvay and Spencer units have been converted from ammonia to methanol production. The ease of this conversion is partially responsible for the rapid production expansion in the postwar period. The Commercial Solvents unit at Sterlington with which this article is primarily concerned was built on the site of a partially completed ammonia plant. The big enigma of the industry is the plant built by Du Pont at Morgan-

town, W. Va., for army ordnance and operated since the war by Heyden Chemical Company. This plant was built as an ammonia plant, readily convertible to methanol synthesis. During the war it produced both products simultaneously. It is rumored to have a total methanol capacity of between 70,000,000 and 80,000,000 gallons annually or about one half of the present national production. Little methanol has been produced at this plant since the war in spite of the marked excess of demand over the ability to produce. It is possible that other factors make operation of this plant for methanol production impractical. If this plant were to begin operations at capacity the methanol supply picture might be altered overnight.

Technologically the most significant recent trend in methanol synthesis has been that from water gas to natural gas as a source of synthesis gas to be fed to the converters. At the end of the war in 1946, 71% of the carbon monoxide used for the synthesis of methanol was obtained from coal or coke. This year an estimated 77% (*34*) will be derived from reformed natural gas. All but one of the plants built since the war are based on a natural gas feed, and are located in the Southwestern oil and gas field area. Economic considerations primarily are responsibile for the changeover. However, the economic advantage of synthesis from natural gas may prove to be transitory. Within the post World War II period natural gas prices, f.o.b. wellhead, have been increased from 1 to 3 cents to 6 to 9 cents. Economic Cassandras have predicted that the climb may go on to as much as 18 cents. At somewhere near this level the coal–natural gas economics may again balance in certain areas where low cost coal is available.

STERLINGTON METHANOL PLANT

Of the gas-based installations the easternmost, and hence the closest to the large marketing centers, is that of Commercial Solvents Corporation at Sterlington, La., on the site of what was once the Dixie Ordnance Works. This plant is built on foundations that were intended for an ammonia synthesis plant. The reformer furnace, some of the compressors, a few tanks, towers, and partially finished buildings were salvaged from the incomplete ammonia unit. However, the plant cannot be considered as having been converted from the ammonia unit.

The Dixie ordnance plant was originally authorized, in August 1941, to produce 150 tons of ammonia per day. In March 1942 before the original unit was completed the authorization was increased to 600 tons. Rather than attempt to enlarge the partially completed unit or design an additional 450-ton unit the construction contractor, The M. W. Kellogg Company, began the construction of three additional units from the design specification for No. 1. However, 6 months later, in September 1942, the authorization was halved and construction on Nos. 3 and 4 units was halted. Only the concrete footings for these units were completed. These footings remain unused on the present plant site. No. 1 unit was completed and in production by April of 1943. The following month authorization for the partially completed No. 2 unit was canceled and construction was suspended. At that time, No. 2 unit was about 80% completed. However, immediately after construction ceased the Ordnance Department, for whom the plant was being built, began to cannibalize the unfinished installation. When Dixie Ordnance Works closed down on the day after V-J Day, little remained of No. 2 unit but the most immovable equipment. The unfinished compressor building remained standing but the gantry crane over the converters had been sold and its supporting structure cut up for scrap iron. The converter shells also had been scrapped. Eleven of the original sixteen compressors remained and the reformer and waste-heat boiler were partially completed. There was no distillation unit since it was not required for the production of ammonia.

CONVERSION TO METHANOL PRODUCTION

After the cessation of hostilities, the Commercial Solvents operating crew placed the entire plant in stand-by condition. Mechanical units were partially dismantled and all metal pieces given an oil or grease coating. The plant remained in this condition during sales negotiations between the War Assets Administration and Commercial Solvents. In September 1946 the sales transaction was completed and Commercial Solvents bought the installation as it stood for $5,850,000. It was the original intent of the company to redesign Unit No. 1 so that all or part of it could be employed for methanol synthesis. However, the sustained demand for ammonia as well as the continued scarcity of methanol led company officials to expand these plans. No. 1 unit continued production as an ammonia plant and the remains of the No. 2 unit were built into a 45,000-gallon-per-day methanol plant at a cost of about $5,000,000. This plant went on the line last April and has operated without a major shutdown since that time.

As completed, the plant is of conventional modern design which differs little from the first commercial scale methanol synthesis plant built in this country in Peoria by Commercial Solvents in 1927 (*35*). This original plant was constructed to utilize gases evolved from the butyl alcohol–acetone fermentation chambers. It has been enlarged since and modified to handle natural gas as is done at Sterlington. Temperatures and pressures are essentially the same in both plants. Important changes have been made only in catalyst basket design and in the installation of automatic process controls.

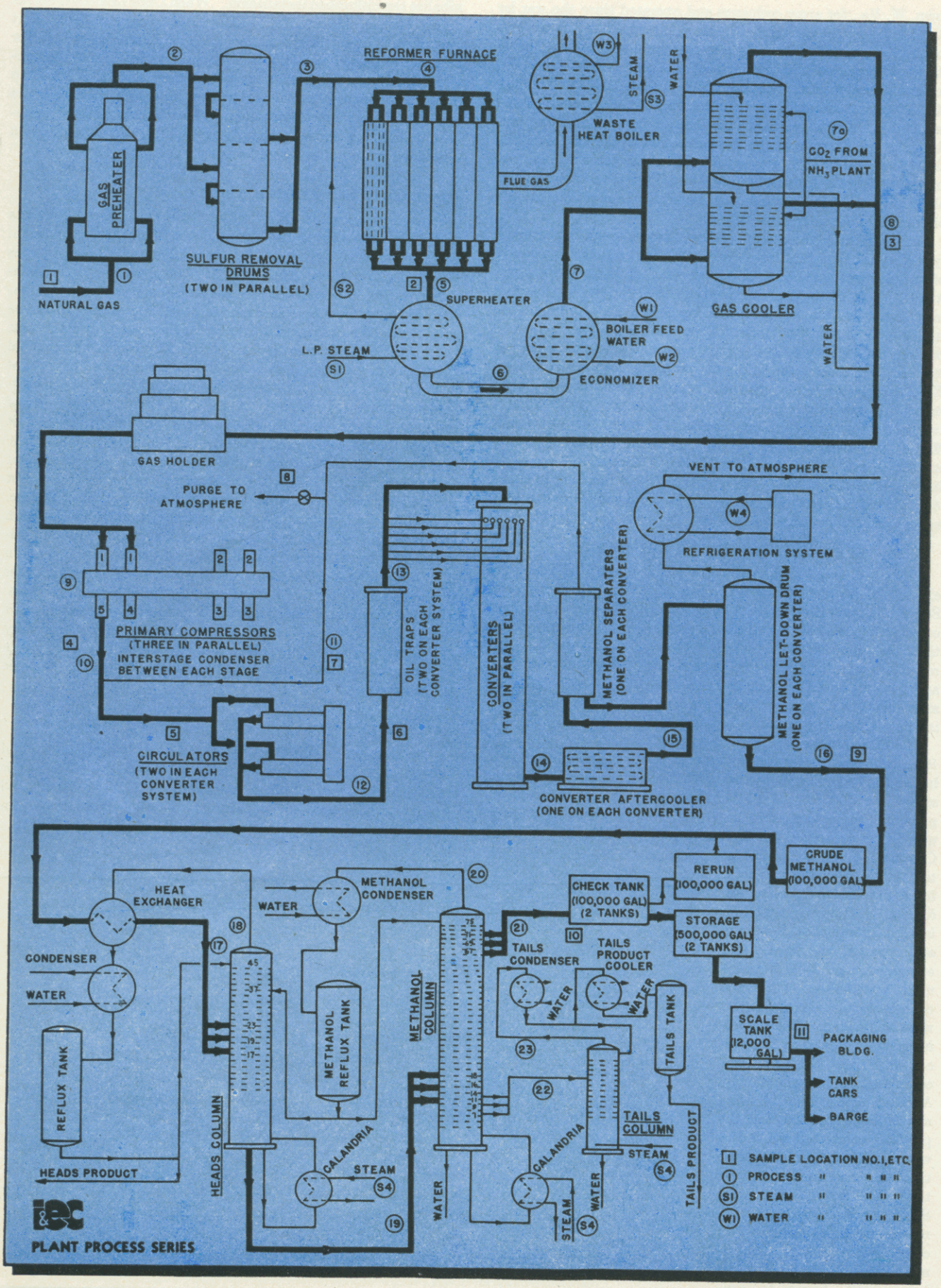
NATURAL GAS SUPPLY

The raw gas for the Sterlington plant comes from an area of Monroe gas fields within 50 miles of the plant. The gas is furnished by two suppliers, Southern Carbon Company and Interstate Natural Gas Company, at a pipe-line pressure of from 35 to 50 pounds per square inch. The gas as delivered is largely

TABLE I. PRESENT PRODUCERS OF SYNTHETIC METHANOL

Company and Location	Method of Production	Raw Materials	Began Operation	Estimated Capacity, Millions of Gallons per Year[a]
Carbide & Carbon				
Niagara Falls, N. Y.	$CO + H_2$	Coke	1929 (1940)[b]	6
St. Charleston, W. Va	$CO + H_2$	Gas	1940	6
Celanese Corporation				
Bishop, Tex.	Oxidation of butane and and propane	Gas	1945	4
Cities Service				
Tallant, Okla.	Oxidation of natural gas (CH_4)	Gas	1929 (1934)[a]	6
Commercial Solvents				
Peoria, Ill.	$CO + H_2$ or $CO_2 + H_2$	Gas	1927 (1932)[a]	3
Sterlington, La.	$CO + H_2$ or $CO_2 + H_2$	Gas	1948	15
Du Pont				
Belle, W. Va.	$CO + H_2$	Coke	1927 (1930)[a]	32
Sabine River (Orange), Tex.	$CO + H_2$	Gas	1948	32
Heyden Chemical Co.				
Morgantown, W. Va.	$CO + H_2$	Coke	1943	75
McCarthy Chemical Co.				
Winnie, Tex.	$CO + H_2$	Gas	1948	2
Solvay Process Co.				
South Point, Ohio	$CO + H_2$	Coke	1948	11
Spencer Chemical Co.				
Military, Kan.	$CO + H_2$	Gas	1948	11

[a] Best available estimates give plant capacity based on 330 producing days per year.
[b] Expanded capacity.


REFORMER FURNACE
GAS PREHEATER
SULFUR REMOVAL DRUMS (TWO IN PARALLEL)
NATURAL GAS
SUPERHEATER
FLUE GAS
WASTE HEAT BOILER
STEAM
WATER
CO2 FROM NH3 PLANT
GAS COOLER
L.P. STEAM
BOILER FEED WATER
ECONOMIZER
GAS HOLDER
PURGE TO ATMOSPHERE
VENT TO ATMOSPHERE
REFRIGERATION SYSTEM
PRIMARY COMPRESSORS (THREE IN PARALLEL) INTERSTAGE CONDENSER BETWEEN EACH STAGE
OIL TRAPS (TWO ON EACH CONVERTER SYSTEM)
CONVERTERS (TWO IN PARALLEL)
METHANOL SEPARATERS (ONE ON EACH CONVERTER)
METHANOL LET-DOWN DRUM (ONE ON EACH CONVERTER)
CIRCULATORS (TWO IN EACH CONVERTER SYSTEM)
CONVERTER AFTERCOOLER (ONE ON EACH CONVERTER)
CRUDE METHANOL (100,000 GAL)
RERUN (100,000 GAL)
CHECK TANK (100,000 GAL) (2 TANKS)
STORAGE (500,000 GAL) (2 TANKS)
HEAT EXCHANGER
METHANOL CONDENSER
TAILS CONDENSER
TAILS PRODUCT COOLER
CONDENSER
WATER
REFLUX TANK
METHANOL REFLUX TANK
METHANOL COLUMN
TAILS TANK
SCALE TANK (12,000 GAL)
PACKAGING BLDG.
TANK CARS
BARGE
HEADS COLUMN
CALANDRIA
STEAM
TAILS COLUMN
TAILS PRODUCT
HEADS PRODUCT
SAMPLE LOCATION NO.1,ETC.
PROCESS " " " "
STEAM " " " "
WATER " " " "
PLANT PROCESS SERIES

OPERATING DATA FOR METHANOL PROCESS

(Numbers correspond to points on flow sheet, Figure 2)

GAS STREAM

		Temperature, ° F.	Pressure, Lb./Sq. In. Gage
1		80	28
2		750	17
3		670	16
4		850	16
5		1260	2.25
6		940	2.25
7		335	2.25
7a		100	5
8		90	0.5
9	1st stage, in	90	0.5
	out	325	45
	2nd stage, in	100	45
	out	360	225
	3rd Stage, in	97	225
	out	310	790
	4th stage, in	100	790
	out	320	2400
	5th stage, in	100	2400
	out	230	4400
10		100	4300
11		97	4300
12		113	4600
13		112	4500
14		300	4340
15		97	4300
16		930	5
17		152	5
18		152	0.5
19		174	4
20		175	1
21		154	...
22		190	6
23		189	2

STEAM SYSTEMS

S-1		350	30
S-2		940	30
S-3		404	260
S-4		350	30

WATER SYSTEMS

W-1		90	...
W-2		120	...
W-3		264	...
W-4		35	...
Flue gas to waste heat boiler		1340	...
Exhaust gas from waste heat boiler		600	...

methane and contains a few objectionable impurities. A typical sample analysis:

	%		%
CH_4	93.18	C_5H_{12}	0.05
C_2H_6	0.55	N_2	5.54
C_3H_8	0.24	CO_2	0.11
C_4H_{10}	0.22	O_2	0.11

The gas comes into the plant through a metering and reduction station. The pressure is dropped through a reducing valve in this station to the maximum pressure which can be maintained uniformly. The pressure is usually between 30 and 35 pounds per square inch gage. The reducing valve is actuated automatically based on downstream pressure. Process gas to the reformers is taken directly from this station. Fuel gas for the boiler furnaces and heaters is run through a second reducing station where the pressure is further reduced to 27 pounds per square inch gage.

SYNTHESIS GAS PREPARATION

The process gas for the reformer is preheated in a spiral tube gas-fired preheater originally installed as an air preheater for the ammonia unit. The gas enters the unit at the bottom and passes through one of two parallel, 225-foot, 5-inch outside diameter spiral tubes. The exit temperature is about 750° F. The heated raw gas then is introduced into sulfur removal drums. Commercial Solvents engineers believe that this purifying step is unnecessary with the present gas supply but it has been included in the design to provide for the processing of high sulfur gas if it becomes necessary. The sulfur removal drums are divided into four compartments, 6 feet 6 inches in diameter and 28 feet deep, filled with extruded, 0.1875 × 0.5 inch, cylindrical pellets of zinc oxide. Purification is effected by the reaction:

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

Four parallel gas paths are available, each passing through two catalyst compartments in series. Two such paths are sufficient to carry the gas flow at normal operating pressures so that ample flexibility is available for clean-out and replacement of adsorbent. The frequency of replacement of adsorbent in these drums will depend on the sulfur content of the gas. With the present supply at Sterlington they will probably be active for many years.

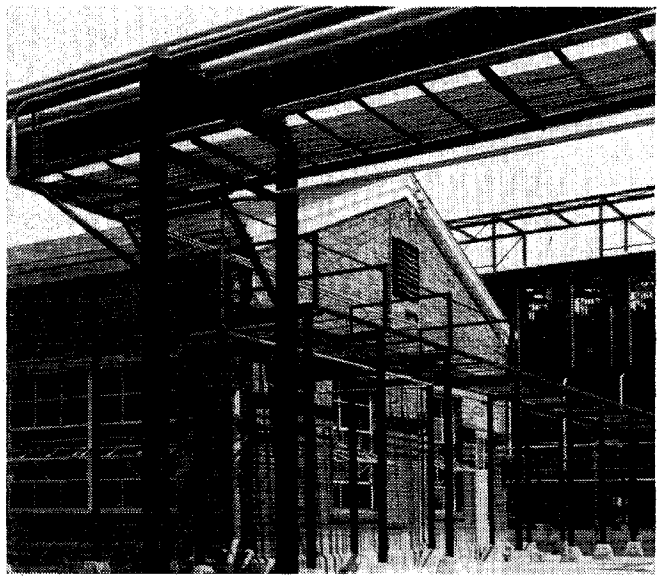
The purified gas is mixed with 30 pounds per square inch gage steam which has been heated to 940° F. in a shell and tube heat exchanger which extracts heat from the reformed gas coming from the reformer furnace. The ratio of steam to gas is set by the operator and then maintained automatically by differential pressure flowmeters on both the gas and steam lines. Mixing is accomplished in a simple T-joint.

The combined gas and steam passes downward in parallel through a bank of 132 catalyst filled tubes arranged in six sections in the reformer furnace. The catalyst used at Sterlington consists of 0.75-inch ceramic cubes impregnated with finely divided metallic nickel. The furnace is gas fired from the top and held at about 1750° F. The flow of fuel gas to the furnace is controlled by the temperature reading of a thermocouple located in the reformed gas outlet. This outlet temperature is held at about 1250° C. Flue gas from the reformer is utilized in a waste-heat boiler to produce 40,000 pounds of 260-pound steam per hour. The waste-heat boiler is a watertube type similar in design to the gas-fired boilers in the plant's main power house.

The reformed gas passes immediately through the steam superheater where its temperature drops to about 950° F. and then is introduced into a boiler feed water heater where it is cooled to 335° F. Both the superheaters and the feed water heater are shell and tube type heat exchangers. Final cooling of the gases is achieved in a bubble cap tower originally intended as a stripper in

Figure 2. Flow Sheet for Methanol Process at Commercial Solvents Corporation Plant, Sterlington, La.

Correction to flow sheet: Total capacity of the two check tanks should be 200,000 gallons. Total capacity of the two storage tanks should be 2,000,000 gallons.
Process data at points indicated are given in table top this page.



Outdoor Pipe Racks, Sterlington Plant

Overhead copper tubes carry gas samples from points throughout plant to analysis laboratory

the ammonia unit. The tower has been divided into two sections used in parallel to increase the effective gas flow area. Each section has eleven trays. The flow of water to the cooling tower is controlled by a thermocouple located in the water outlet. The water stream in the cooler is controlled to hold the temperature below 120° F. to avoid corrosion. The Dixie plant's water supply is obtained from either the nearby Ouachita River or the Bayou Bartholomew. At high water the river water is satisfactory but in the past, as the water level falls, water from the bayou has given the least corrosion trouble. However, during the past season the bayou was sprayed with 2,4-D to destroy the water hyacinths which formerly covered the surface of the bayou. The removal of this flora has affected the corrosive activity of the water. At low temperatures algae form in the systems and at temperatures above 120° F. corrosion becomes severe. Although the boiler feed water for the plant is filtered and passed through ion exchangers, the cooling water is merely settled to remove sludge and chlorinated to inhibit algae growth.

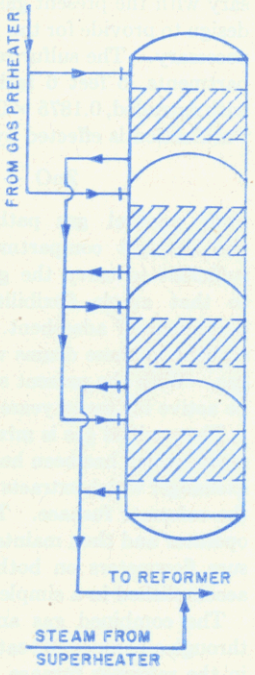


Figure 3. Gas Flow Through Sulfur Removal Drums

ADDITION OF CARBON DIOXIDE

The reaction of steam and methane in the reformer follows the equations:

$$CH_4 + H_2O = 3H_2 + CO \quad (1)$$
$$\Delta H = +49{,}271 \text{ cal. } (19)$$

$$CH_4 + 2H_2O = 4H_2 + CO_2 \quad (2)$$
$$\Delta H = 39{,}434 \text{ cal. } (19)$$

From these reformed gases methanol will be produced by the reactions:

$$CO + 2H_2 = CH_3OH \quad (3)$$
$$\Delta H = -21{,}630 \text{ cal. } (19)$$

$$CO_2 + 3H_2 = CH_3OH + H_2O \quad (4)$$
$$\Delta H = -11{,}850 \text{ cal. } (19)$$

In order for the products of Equations 1 and 2 to react according to 3 and 4 some additional carbon oxides must be provided. At the Dixie plant the deficiency is made up by introducing excess carbon dioxide available as waste gas from the ammonia unit into the gas cooler below the top two plates. Introduction at this point in the stream provides a cursory scrubbing for the carbon dioxide and ensures uniform mixing with the reformed gas.

By adding excess dioxide, Equation 4 is favored; here a mole of water is produced with each mole of methanol. This not only dilutes the product but wastes one third of the hydrogen produced in the reformer. Most synthesis installations are designed to minimize the amount of dioxide in the system and force the synthesis to proceed according to Equation 3. Some units even include a carbon dioxide absorption tower in the cycle to obtain higher purity methanol and minimize refining operations. Synthesis from pure carbon monoxide gives about 95% methanol. Mixtures of mono- and dioxide generally yield about 80% methanol.

However, Equation 3 is more highly exothermic than 4 and frequently produces hot spots in the catalyst mass. The temperatures attained in these hot spots are sufficient to initiate the even more highly exothermic methanation reaction which reconverts the reformed gas to methane. Aside from the loss of production entailed in this side reaction it is inclined to run away with the process and sometimes can be halted only by shutting down the converter.

Because of these disadvantages in the use of the monoxide reaction Commercial Solvents, since their pioneer installation at Peoria, have used the synthesis from dioxide. Additional dioxide in the converter feed has a quenching action and affords a simple means of controlling the speed and temperature of the synthesis reaction.

The mixture of reformed gas and carbon dioxide from the gas cooler flows to a 1,000,000-cubic foot capacity, three-lift gas holder, where it is held until required by the synthesis unit.

COMPRESSOR CYCLE

A 30-inch gas line leads from the gas holder into a 42-inch header which feeds the first stages of the primary compressors. The three compressors, arranged in parallel, compress the synthesis gas from holder pressure to about 4500 pounds per square inch gage in five stages. They were manufactured by Clark Brothers and are driven by 8-cylinder Clark-Skinner Uniflow steam engines developing 2700 h.p.

The eight steam cylinders are mounted vertically in a single row. Compressor cylinders are placed horizontally on both sides of the power cylinders; all cylinders are connected to one crankshaft. Two first-stage and two second-stage compressor cylinders are located on one side and two third-stage, one fourth-stage, and one fifth-stage on the other.

The steam engines operate at 26 inches of mercury vacuum, maintained by Croll-Reynolds countercurrent barometric condensers and two-stage ejectors with barometric intercondensers.

Each compressor is supplied with intercoolers and knockout drums for oil and water, between each stage, and after the fifth-stage. The interstage units are located outside the compressor house as safety precaution.

Because of the toxic nature of the carbon monoxide contained in the synthesis gas the stuffing boxes of the compressors are covered by suction hoods connected to a 5600-cubic foot per minute capacity fan vented to the outside atmosphere.

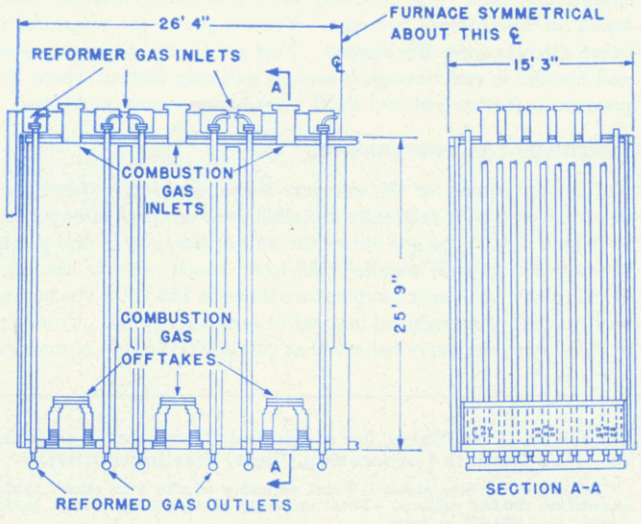


Figure 4. Diagram of Gas Reformer Furnace

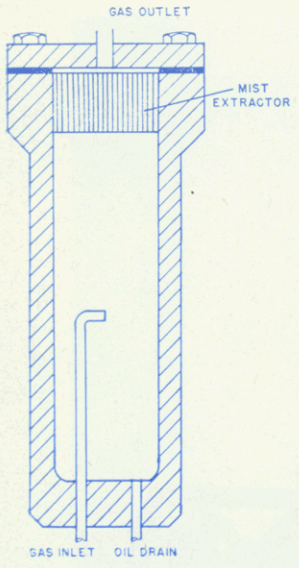


Figure 5. Circulator Oil Trap

The compressor house which contains the primary compressors and the circulators is provided with a high capacity ventilating system to ensure against the building up of carbon monoxide in the atmosphere. Eight fans, each having a capacity of 15,000 cubic feet per minute, force air through the 800,000-cubic foot compressor area providing nine complete air changes per hour.

The high pressure gas from the three compressors enters a common manifold where it combines with recirculating gas from the converters and enters the recirculating compressors, called circulators. The four circulators are single-stage, with two vertical steam cylinders, and two horizontal compressor cylinders on one side. These engines also operate at reduced pressure; the vacuum systems are similar to those for the primary compressors.

CONVERTER SYSTEM

Since the converters are estimated to have about 12 to 15% per pass conversion efficiency, new make-up gas comprises only about 15% of the feed to the recirculating pumps. Two circulators operate in parallel for each converter system to raise the gas pressure to the operating level of about 4800 pounds per square inch gage. Each pair of circulators discharges to a common line which leads to two parallel oil traps which remove the last traces of nongaseous impurities from the synthesis gas before it enters the converter.

The outlet line from the two oil traps of each circulating system is divided into a main feed to the top of the converter, a by-pass to the bottom of the converter, and quench lines which are introduced at various points to permit close control of conversion temperature. All lines are controlled by valves operated from a control panel inside the compressor building.

The introduction of cold gas into the catalyst bed for temperature control as practiced at Sterlington is a common practice and is known to have been employed in German synthesis plants (*26*). However, an interesting variation has been reported wherein water is injected into the synthesis gas stream to control the temperature in the convertor (*7*). In addition to the localized cooling provided by the quench lines the over-all temperature of the converter chamber can be lowered by increasing the rate of gas flow and/or decreasing the operating pressure.

The main stream of synthesis gas from the control station flows to the top of the converter, downward through the annular space between converter shell and catalyst basket, through the shell side of the converter exchanger, upward through the tubes imbedded in the catalyst, downward through the catalyst beds, through the tube side of the interchanger, and out the bottom of the converter to a water cascade condenser. The first pass serves both to cool the catalyst bed and to preheat the reactor gas. Actual conversion occurs on the third pass (*9*).

The Commercial Solvents installation operating at about 5000 pounds per square inch gage pressure and 400° C. is a relatively high temperature and low pressure unit. Current practice in methanol conversion ranges from 2200 to 14,700 pounds per square inch gage and 250° to 400° C. (*16*, *26*). In general, per cent conversion varies inversely with the temperature and directly with the pressure. Optimum conditions are reported to exist in the temperature range 300° to 400° C. (*21*).

Condensed methanol and unreacted gases from the after-cooler flow to a methanol separator where separation of the gases and product methanol is made. This separator is similar to the oil traps mentioned above. Recycle gas flows from the top of the separator drum to the suction of the circulators. A Statham strain gage and an automatic variable orifice bleed-off valve are introduced into the recycle line to maintain a constant pressure in the line and consequently in the converter. If there were no purging done at this point the concentration of nonreacting gases in the converter would increase steadily thus increasing the pressure in the converter system. The purge gas consists of unconverted carbon mono- and dioxides and hydrogen as well as uncracked hydrocarbons and nitrogen. It is led from the purge valve to the power boiler fire boxes to recover the fuel potential present. Liquid methanol product flows by mechanical liquid level control to the letdown drums from whence it is pumped through positive displacement meters to intermediate storage tanks.

CONVERTER AUXILIARIES

An external refrigeration system, having a capacity of 130,000 B.t.u. per hour, is provided to condense the vapors vented from the letdown drums. This refrigeration unit is unique with the Sterlington plant. In northern installations where cooling water temperatures can be maintained around 60° F. so little condensable material passes through the after coolers that product loss from the letdown drum vent is negligible. However, at Dixie, cooling water temperatures often reach 80° F. which does not completely condense the lower boiling converter products. The present experimental installation is designed to maintain a temperature of 35° F. in the vent condenser.

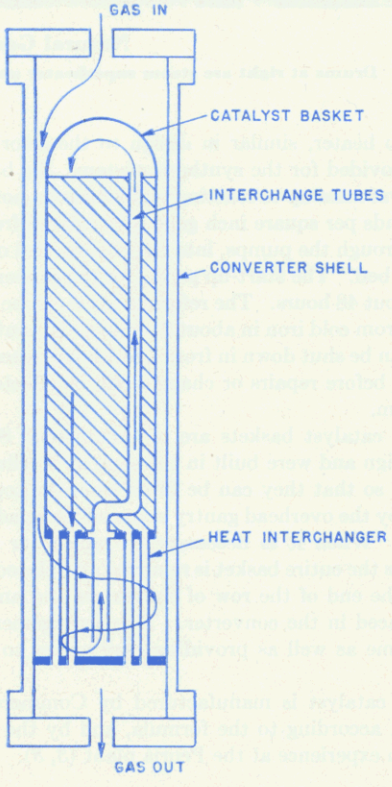
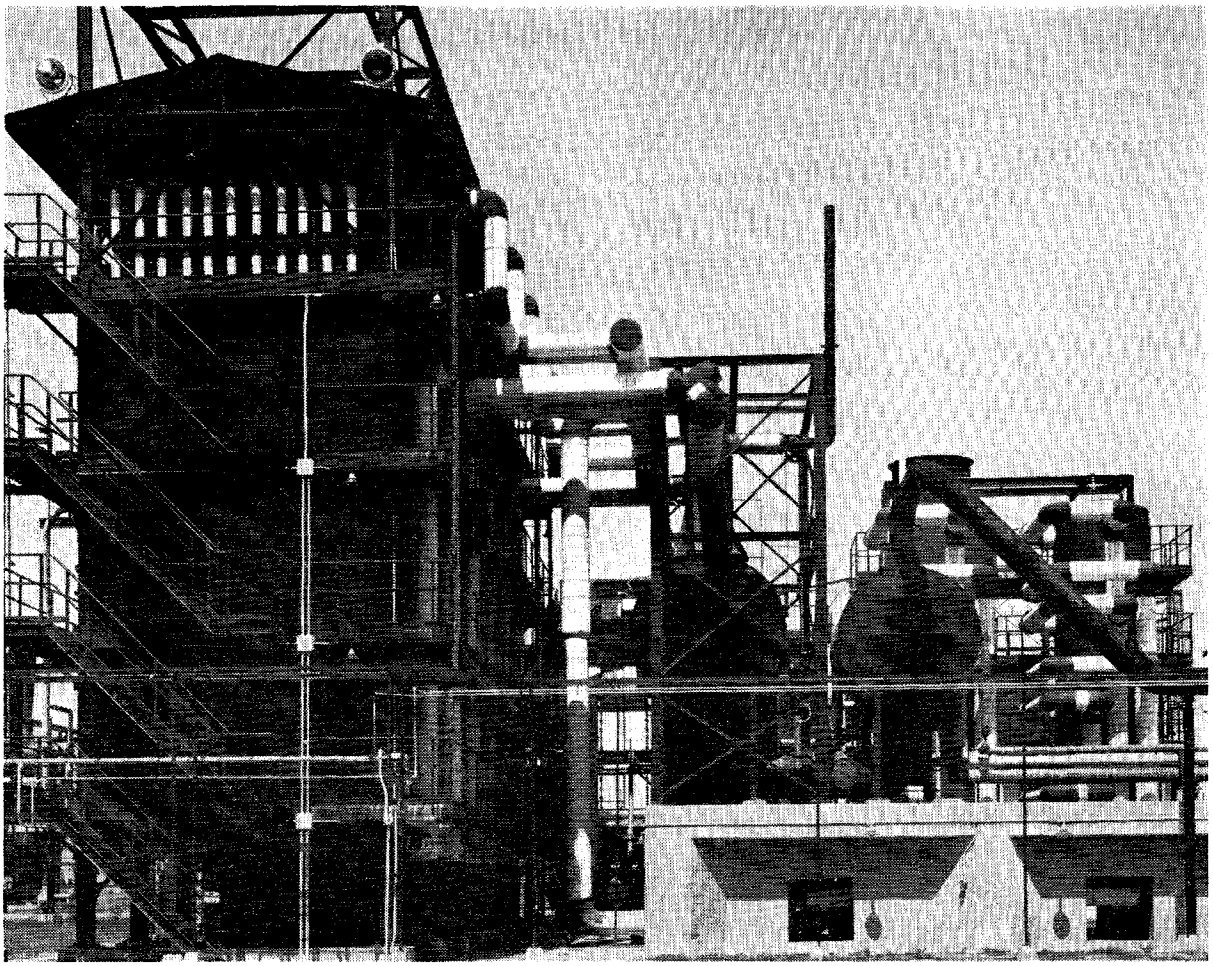


Figure 6. Schematic Diagram of Gas Flow Through Methanol Synthesis Converter



Natural Gas Reformer Furnace, Sterlington Plant

Drums at right are steam superheater and heat exchanger; vertical drums in background are sulfur removal units

A start-up heater, similar in design to the reformer gas preheater, is provided for the synthesis system. To bring the converter catalyst mass up to reacting temperature a nonreacting gas at 2500 pounds per square inch gage is circulated from the start-up heater through the pumps, into the bottom and out the top of the catalyst bed. The start-up period for the converter system is normally about 48 hours. The reformer cycle can be brought into production from cold iron in about 24 hours. In contrast the synthesis line can be shut down in from 3 to 4 hours whereas 24 hours are required before repairs or changes can be effected on the reformer system.

Converter catalyst baskets are of Commercial Solvents Corporation design and were built in the shop at Sterlington. They are designed so that they can be lifted from the top of the converter shell by the overhead gantry crane which straddles the converter area. When it is necessary to replace or examine the catalyst mass the entire basket is removed and placed in a vertical support at the end of the row of converters and another loaded basket is placed in the converter. This arrangement minimizes shutdown time as well as providing easy access to the catalyst mass.

Methanol catalyst is manufactured by Commercial Solvents Corporation, according to the formula, and by the methods developed from experience at the Peoria plant (*3*, *8*).

REFINING BY DISTILLATION

The crude methanol from the intermediate storage tanks is distilled in an E. B. Badger & Sons Company continuous refining unit. The still is designed to produce 57,000 gallons per stream day of finished product based on a crude feed of 76,000 gallons per day containing:

	%
Methanol	74.7
Heads	0.1
High boilers (tails)	0.2
Water	25

The refining unit is comprised of three separate columns. Crude methanol feed to the first column is preheated in a shell and tube exchanger heated by the overhead take-off and introduced between the 17th and 24th tray of the 45-tray column. The column is heated by 35-pound steam through a closed calandria cut in below the last tray. The overhead discharge from this column is essentially a mixture of dimethyl ether with other ethers and some methanol. After passing through the heat exchanger and being condensed in a shell and tube type water cooled condenser most of it is returned to the top of the column to maintain a 20 to 1 reflux ratio. The net overhead representing about 2.5% of the total product is pumped to heads storage. To date no practical use has been found for this by-product at Sterlington and the fraction is being accumulated in storage tanks.

The bottoms from the heads column are pumped direct to the methanol column. This is the largest of the three columns, having 75 trays. It is heated by a closed calandria like the heads column. The feed is introduced between the 14th and 19th tray. Product methanol is taken off between the 67th and 73rd tray. The overhead from this column is condensed in a water cooled condenser and used as reflux to maintain a reflux ratio of 1.75 to 1.

TABLE II. ANALYSES PROCEDURE

	Location	Frequency	Apparatus	Tested for
A-1	Natural gas supply	Periodic	Low temperature Podbielniak column	H_2, CH_4, C_2H_4, C_3H_8, $C_4H_{10}C_5H_{12}$, N_2, CO_2, O_2
A-2	Exit gas from reformer	Each shift	Burrell gas analyzer	CO_2, CO, H_2, CH_3, N_2
A-3	Exit gas from gas cooler	Continuously	Thermal conductivity cell	CO_2
A-4	Compressed gas from compressors	Several times per shift	Burrell gas analyzer	CO, CO_2, H_2, H_2O
A-5	Make-up gas	Several times per shift	Burrel gas analyzer	CO, CO_2, H_2, H_2O
A-6	Gas to converter (make-up plus recycle)	Several times per shift	Burrell gas analyzer	CO, CO_2, H_2, H_2O
A-7	Gas from converter (recycle)	Several times per shift	Burrell gas analyzer	CO, CO_2, H_2, H_2O
A-8	Purge gas	Occasionally	Burrell gas analyzer	CO, CO_2, H_2, H_2O
A-9	Crude product methanol from each converter	Hourly	Specific gravity	Organic solvent content
A-10	Check tanks	Hourly	.....	CH_3OH (99.8% plus) Sp. gr. (0.792–0.793 at 20° C./20° C.) Acidity (<0.01% as formic acid) Alkalinity (no color with phenolphthalein) Color (water white) Dist. range (64–66° C.) Acetone (<0.03%) Nonvolatiles (<0.002 g./100 cc.) $KMnO_4$ test (color retained at 60° F. for 30 min.)
A-11	Loading	Each customer shipment		

A small amount of overhead is drawn off and added to the heads column reflux to prevent the accumulation of excessive light product in the main column. Most of the water in the converter product is removed as bottoms from this column.

A side cut is also taken below the inlet between the 7th and 12th tray. A typical analysis of this product is:

%	
30	Methanol
20	Isopropyl alcohol
25	Isobutyl alcohol
6	5+ carbon alcohols
19	Water

Traces of ethers, ketones, and aldehydes also are sometimes present. This tails cut is introduced at the 14th tray of a steam stripping column having 21 trays. Heat is provided by the introduction of open steam to the bottom of the column. By controlling the operating condition of this column so that the steam does not carry through the trays most of the water taken off with the tails can be eliminated. All components of the tails cut boil below 100° C. The overhead from the stripper is condensed in a water cooled condenser and then cooled in a Graham Heliflo cooler before being pumped to storage. Tails product also has been collected at Sterlington (pending the development of an economic use for the material) since the plant went into operation. The most promising possibility seems to be esterification to produce technical acetates.

LOADING AND SHIPPING

The product methanol from the main tower is collected in check tanks where it is analyzed for quality. If it meets specifications, it is pumped to one of the 1,000,000-gallon final storage tanks. Material which does not meet specifications is pumped to a rerun tank for redistillation.

Loading and shipping operations are concentrated in a building originally intended as a power house for No. 2 unit. Two railroad sidings are located west of this building for tank car methanol loading. Recently antifreeze canning equipment has been installed in this building. This addition will permit the filling of 60 quart cans per minute and 27 gallon cans per minute. Facilities for filling 5-gallon cans and 55-gallon drums have been installed also. A 100,000-pound tank scale and 12,000-gallon scale tank are installed in the building. Methanol is pumped from finished storage tanks to scale tank for weighing, thence to the tank car loading rack.

A dock is available on the Ouachita River so that barges can be loaded direct from the scale tanks through a 6-inch loading line.

Utilities for the methanol plant are supplied in general by facilities common to it and the adjacent ammonia plant.

INSTRUMENTATION

Extensive instrumentation with accompanying automatic controls has made it possible to produce 45,000 gallons of methanol per day at Sterlington with about half the labor force necessary at the 10,000-gallon per day Commercial Solvents plant at Peoria. Automatic control of the synthesis system of the process is particularly ingenious.

Most gas flowmeters in the Dixie plant operate by measuring the pressure drop through a fixed orifice. Assuming the density and other physical factors of the flowing fluid to remain constant, the rate of flow through such an orifice varies with the square root of the differential pressure across the orifice. Automatic control valves are of the air-actuated diaphragm type. Temperature measurement is entirely by thermocouple.

The introduction of thermocouples into the converter catalyst mass presents particular difficulties. The thermocouple well must penetrate both the basket in which the catalyst is sealed and the pressure containing wall of the converter shell. Because of these requirements there is approximately 0.75 inch of metal interposed between the couple and the catalyst mass in which the temperature is being measured. As a result there is an appreciable lag between temperature changes in the catalyst and the response of the temperature recorder. Because of this lag other installations have reported that instantaneous localized hot-spots have occurred in the catalyst, hot enough to melt completely portions of the copper contained in the basket without producing a detectable deviation in the temperature record.

In the Commercial Solvents plants at Sterlington and Peoria, the thermocouples are inserted through the head of the converter shell. In the Peoria units provisions are made for moving the couple through the length of the catalyst bed but no such arrangement was considered necessary in the newer installation. Temperatures are measured at 68 points in the catalyst baskets and 8 points on the exterior of the converter shells at Dixie.

Pressures are measured throughout the high pressure system by Bourdon tubes. All compressors are equipped with automatic cutouts operated by lubricating oil pressure as well as emergency switches located at strategic points in the compressor house; any or all of the compressors can be stopped instantaneously. A safety device also is installed on the reforming furnace which actuates an alarm if the furnace temperature exceeds a maximum of 1500° F.

Automatic liquid level controllers are mechanical float type throughout the plant. However, bubbler type, direct reading indicators are used to indicate the still reservoir levels in the control house and all methanol holding tanks are equipped with both float and bubbler type meters.

Instrument indicators are centralized at two control boards. The entire gas reforming operation and the distillation of the products of the converters can be monitored and controlled from a station in the control house. A second control station from which the converter operation can be followed and adjusted is located in the compressor house. It is not necessary to have an

operator continually present at these stations because under normal conditions the process proceeds automatically.

CHEMICAL CONTROL

Chemical analysis of the gas stream is made at all critical points on the process. A continuous stream of reformed gas is taken from the gas cooler and passed through a thermal conductivity meter in a building near the reformer furnace to determine the carbon dioxide content. This reading is used to determine the quantity of dioxide which will be added to maintain the optimum synthesis gas composition in the gas holder. The analyzer is connected to a valve which automatically controls the flow of carbon dioxide being added in the gas cooler. Because of the critical nature of the reformer gas carbon dioxide content, results of the thermal conductivity analyzer are recorded on both of the control panels.

Analyses at other test points are made periodically. Copper or stainless alloy tubes of 0.125-inch outside and 0.03125-inch inside diameter conduct samples from these points to two central locations where Burrell gas analysis apparatus is set up permanently.

The lines dead-end in a sampling valve at the analyzer but because of their small internal diameter can be purged to give a current sample in a maximum of 3 minutes. Samples from any part of the plant can be analyzed at either of the two analyzer locations.

The instrument maintenance crew at Sterlington consists of six men under the supervision of the instrument engineer. This crew divides its time between the ammonia and methanol units. By following a regular schedule of check-ups and overhauls for every instrument it has been possible to eliminate shift work in the instrument crew. The entire force works on the day shift under the direct supervision of the engineer in charge. This arrangement has a particular advantage in an outlying district such as Sterlington where almost all instrument technicians must be trained on the job. The system has proved superior to the conventional shift system in terms of both personnel requirements and continuity of production. Emergency night calls have been negligible even though the methanol plant has only recently achieved routine production.

MAINTENANCE PROCEDURE

A well defined maintenance procedure has been devised for the Dixie plant. The mechanical departments which include maintenance, storerooms, toolrooms, and salvage are, like the power and utility facilities, common to both the ammonia and methanol units. To ensure effective accounting and administrative control without incurring excessive protocol, maintenance and repair jobs are divided into two categories. Jobs which will not increase the capital account of the plant are initiated by means of work requests prepared by the operating department head or foreman and submitted to the plant engineer for approval. For major repair or maintenance jobs and for all purchases of material and interdepartment equipment transfers, job orders must be prepared with the approval of major plant and company officials.

FUTURE OUTLOOK

After 6 years of methanol shortage, present indications are that supply finally will balance demand sometime in 1949. All new plants and expansion plans announced for the postwar period will be completed this year and may be expected to be in normal capacity production throughout next year. Estimates vary as to the ultimate total capacity of all installations (*15, 27, 28, 34*) but it is probably safe to assume that total output will be close to 175,000,000 gallons. With production apparently limited to nine companies there is little likelihood that proprietary catalysts will enter the field, and it may be assumed that the producers will continue to manufacture their own catalysts by essentially secret processes.

Natural methanol production has apparently stabilized on a plateau supported by United States Treasury regulations which require the use of wood alcohol in denaturing formulas No. 1, No. 1 Special, and No. SC 2-A. It is unlikely that the volume of production will increase beyond the denaturing requirements unless there is a sudden increase in demand for other wood chemicals.

With the change-over from coal gas to natural gas as a source of carbon and hydrogen the synthetic methanol industry has become independent of the fluctuations in coal production and market price. This will prevent a recurrence of the production lag experienced during the coal strike in 1946. It also will tend to peg methanol prices to natural gas and indirectly to crude oil prices rather than to those of coal and coke. If Fischer-Tropsch synthesis of liquid fuels becomes commercially important, methanol producers will be faced with the necessity of competing with the gasoline producers for the available gas supply. However, they also stand to benefit indirectly from this program if the fluid catalyst techniques perfected for fuel production from synthesis gas prove to be adaptable to the production of methanol.

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